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Effect of Oxygen on Metathesis of *cis*-2-Pentene by a Binary Catalyst System of $W(CO)_5P(C_6H_5)_3$ and $(C_2H_5)AlCl_2$

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Metathesis of *cis*-2-pentene has been studied with the catalytic system $W(CO)_5P\phi_3$, $EtAlCl_2$. Oxygen has a drastic promoting effect on the catalytic system which exhibits, after O_2 introduction, a very high efficiency for metathesis of internal as well as α-olefins. Whereas no significant interaction occurs between $W(CO)_5P\phi_3$ and $EtAlCl_2$, O_2 activation induces slow departure of two carbonyl groups. It is at the beginning of the release of CO that the system is the most active. Spectroscopic studies (uv, ir) indicate at this stage a complexing of a Lewis acid to the terminal oxygen of the *trans*-carbonyl group of $W(CO)_5$ $P\phi_3$, with a net decrease of the electronic density of W, so that the strength of the W-CO bonds of the square plane is considerably lowered.

It is therefore suggested that the main effect of O_2 is to enhance the Lewis acidity of $EtAlCl_2$, so as to favor an electrophilic attack of the Lewis acid to the tungsten through the carbonyl ligand.

INTRODUCTION

The disproportionation of olefins, discovered in 1964 by Banks and Bailey (*1*) in the heterogeneous phase, can be performed in the homogeneous phase (metathesis) with complexes of molybdenum, tungsten or rhenium associated to various cocatalysts such as alkyl aluminum compounds, butyl lithium or Grignard compounds (*2*). Although many mechanisms have been postulated concerning the role of the catalytic system (*3–5*), the metathesis reaction is far from being fully understood, especially if one keeps in mind that complexes of W^{6+} as well as W^0 are active precursor complexes (*6*), that typical Lewis acids ($AlCl_3$) as well as strong reducing agents (*n*-Bu–Li) can be used as cocatalysts with the same complex WCl_6. It seems, therefore, that a general theory able to explain all the results cannot be advanced and it is necessary to study each catalytic system separately before going further in a mechanistic way. In our laboratory, *cis*-2-pentene disproportionation is being studied both in the heterogeneous (*7*) and the homogeneous phase. In this paper, we report the first results obtained with the catalytic system $W(CO)_5P(C_6H_5)_3$, $(C_2H_5AlCl_2)$, O_2.

The promoting effect of oxygen-containing compounds is well established now in the case of the ring opening polymerization of cycloolefins with catalysts of the type WCl_6, R_3Al. It is generally assumed (*8*) that metathesis and cycloolefin polymerization proceed by a common transalkilidenation mechanism. The compounds which show particularly high activity contain an epoxide group or a hydroperoxide or an alcohol (*9*). Ramaln and Trambouze (*10*) reported the O_2 effect on metathesis of *cis*-2-pentene for the catalytic system $W(CO)_5P(C_6H_5)_3$, $(C_2H_5)AlCl_2$ and, at the same time, Uchida *et al.* (*11*) reported a similar effect in the cases of WCl_6, $(C_2H_5)_3$-Al and $ReCl_5$ $(C_2H_5)_3Al$. We believe, therefore, that the promoting effect of O_2

on metathesis is not specific to our own catalytic system which consists of zerovalent tungsten complex, but that O_2 is a third component, the role of which has to be determined in a mechanistic way.

Experimental Methods

1. *Materials*

The complex of zerovalent tungsten $W(CO)_5P(C_6H_5)_3$ was obtained by mixing stoichiometric amounts of $W(CO)_6$ and $P(C_6H_5)_3$ in a glass tube, which was then sealed. The mixture was heated at 150°C for 1 wk and the product was crystallized in a mixture of ethanol and chloroform. The purity was determined by chemical analysis and infrared spectroscopy (*14*).

$(C_2H_5)AlCl_2(EtAlCl_2)$ was supplied by the Ethyl Corp. It was purified by vacuum sublimation, diluted in anhydrous chlorobenzene (or in hexane) and stored under argon.

Chlorobenzene had a commercial R.P. grade. It was distilled twice over P_2O_5 and under Ar. It was stored under Ar.

cis-2-Pentene had a purity of 95% (with about 5% of the *trans* isomer). It was distilled over Na and stored under Ar.

2. *Apparatus and Procedure for Kinetics Experiments*

The apparatus used for kinetics experiments included a batch reactor in glass with valves allowing argon purge, evacuation, introduction of the various reagents, and eventually circulation of the solution in spectroscopic cells. Various gas syringes as well as burettes allowed given amounts of pentene, O_2, alkyl aluminum or solvent (chlorobenzene) to be introduced into the reactor. A sampling valve was connected to the reactor in order to analyze the gaseous phase at any time of the reaction.

Analysis of the reagents, mainly *cis*- and *trans*-2-butene, *cis*- and *trans*-2-pentene, *cis*- and *trans*-3-hexene, was carried out with a flame ionization chromatograph IGC 15. A 9 m column of 25% weight fractonitrile deposited on embacel was used at 25°C with nitrogen as carrier gas. Analysis of ethylene, ethane, CO, O_2, Ar, was made with a catharometer as detector with three columns, viz., Porapak, molecular sieves at 25°C and molecular sieves at −78°C.

As pointed out by Wang, Menapace and Brown (*12*), the procedure used to perform the experiments is important since variations of the order of introduction of the compounds constituting the catalytic system may give rise to very drastic changes in catalytic activity. For this reason these parameters are reported in the Results. Let us mention here that in most cases $W(CO)_5P\phi_3$ was introduced first into the reactor which was evacuated and carefully purged with argon before the solvent was introduced.

Most of the experiments were carried out at 25°C with concentrations of $W(CO)_5P\phi_3$ and $EtAlCl_2$ of 6×10^{-3} and 21×10^{-3} moles liter^{-1}, respectively, and ratios olefin/W and O/Al equal to 100 and 3, respectively.

The rate of metathesis was estimated from the conversion taken 4 min after *cis*-2-pentene or O_2 introduction depending on the order of introduction of the reagents.

3. *Spectroscopic Studies*

The infrared spectra were recorded on a Perkin-Elmer 125 spectrophotometer from 4000 to 400 cm^{-1}. The spectra were determined with a KBr variable space cell and with solvent in the reference cell.

The electronic spectra were recorded from 200 to 1000 nm with an Optica (Milano) CF4DR double beam spectrophotometer, using CaF_2 (UVF) variable space cells or spectrosil 1.0 mm path length cells. A solvent reference blank was used. During the reaction, the liquid phase was circulated from the reactor to the spectroscopic cells (carefully purged with dry argon) by means of a peristaltic pump.

Results and Interpretations

1. *Characterization of an Active Catalytic System*

The system $W(CO)_5P\phi_3(W)$, $EtAlCl_2$ (Al) exhibited almost no catalytic activity for *cis*-2-pentene metathesis at room temperature. This was the case for various ratios Al:W, olefin:W and for different orders of introduction of the reagents W, Al, olefin. In a typical experiment at room temperature, for ratios Al:W = 4 and olefin:W = 100, the conversion of *cis*-2-pentene to butenes and hexenes reached a value of 5% in 22 hr.

A drastic change in catalytic activity was observed after introduction of molecular oxygen (O:Al = 3) in the system $W(CO)_5$-$P\phi_3$, $EtAlCl_2$, *cis*-2-pentene. This promoting effect of O_2 is illustrated in Fig. 1. In less than 4 min following this introduction, the conversion to butenes and hexenes reached a value of 25% and the equilibrium of 50% conversion was attained in less than 50 min. It is interesting to notice that the introduction of O_2 favored the isomerization of *cis*-2-pentene to *trans*-2-pentene. The ratio *trans*-2-butene to *cis*-2-butene was in favor of the *cis* isomer at the beginning of the reaction, where the conversion was relatively low. This ratio increased with time reaching almost the thermodynamic value for butenes (without butene-1 or isobutene).

The stage at which O_2 was introduced proved to be important. When O_2 was introduced last, the system exhibited always the same high efficiency. For example, the following sequences: pentene–W–Al–O_2, W–Al–O_2–pentene or Al–W–pentene–O_2 gave the same results. However, if $EtAlCl_2$ was oxidized first and the mixture then contacted with the system W + pentene, the rate of metathesis depended on the duration of this oxidation: the longer the oxidation time before mixing, the slower the rate of metathesis. After 5 min of oxidation, the rate of metathesis was decreased four times, whereas after 5 hr of oxidation of the aluminum alkyl, no more catalytic activity was observed.

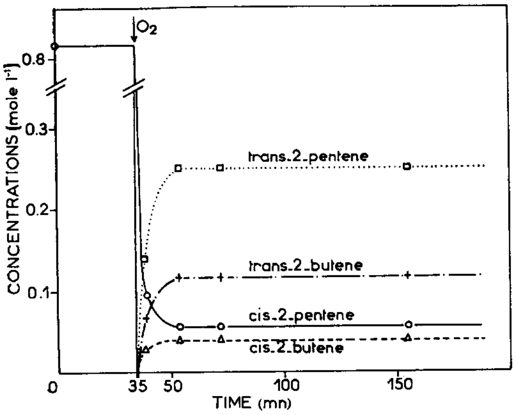


FIG. 1. Promoting effect of O_2 on metathesis: conversion of *cis*-2-pentene to butenes and hexenes as a function of time.

It is therefore obvious from these results that the introduction of O_2 to the system $W(CO)_5P\phi_3$, $EtAlCl_2$ is at the origin of the catalytic activity. Moreover, it is an intermediate species, Al#, produced during the oxidation of $EtAlCl_2$ which is responsible for this activity and not the final product of oxidation $(EtOAlCl_2)_n$.

2. Effect of O_2 on the System $W(CO)_5P\phi_3$, $EtAlCl_2$

These experiments were carried out in the absence of 2-pentene. The procedure was the following. A given amount of $W(CO)_5P\phi_3$ was introduced into the reactor. After evacuation and argon purges, $EtAlCl_2$ was added so that the ratio Al:W ranged between 0.3 and 30. O_2 was then allowed to react with the system (O:Al = 3) and the gases evolved were analyzed by gas chromatography.

Ethane representing 15% of the $EtAlCl_2$ was instantaneously produced. Simultaneously, but with a much slower rate, CO was evolved as shown in Fig. 2. When the ratio Al:W was higher than ca. 1, the curve leveled off at a value of about 2CO/W. The initial rate of CO evolution was estimated from the slopes of the curves of Fig. 2. It was found to depend on the amount of aluminum alkyl initially present. The order with respect to $EtAlCl_2$, obtained by plotting the logarithm of the rate versus the logarithm of $EtAlCl_2$ concentration, was found to be equal to 0.9.

At this stage of our experiments, we wondered whether it was the same active aluminum species, Al# (produced during the oxidation of $EtAlCl_2$), which was at the origin of the CO evolution and of the catalytic activity. One might suppose that both phenomena are connected and we tried therefore to determine the rate of metathesis at various stages of CO evolution.

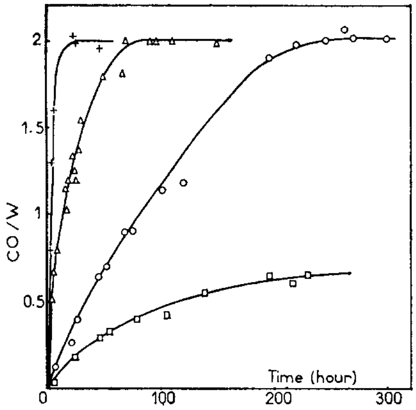


FIG. 2. Amount of CO released upon O_2 introduction as a function of time for various ratios Al/W: (□) 0.3, (○) 1, (△) 4, (+) 30.

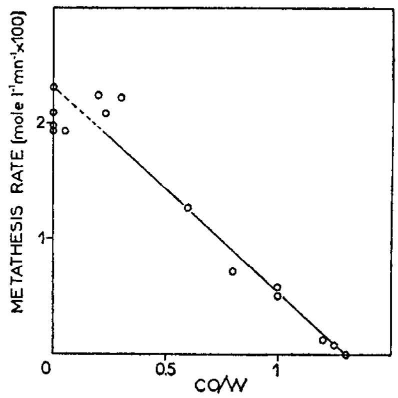


FIG. 3. Rate of metathesis at various stages of CO evolution.

3. *Catalytic Activity During CO Evolution*

These experiments were conducted in the following way. $W(CO)_5P\phi_3$ and $EtAlCl_2$ were introduced into the reactor with the ratio Al:W = 4. Then a known amount of O_2 such that O:Al = 3 was allowed to react. For a given experiment *cis*-2-pentene was introduced into the reactor (C_5:W = 100) when a given ratio of CO:W (determined by chromatographic analysis) was attained. The catalytic activity (Fig. 3) was then determined. If we except the results obtained at the very beginning of the evolution (up to 0.2 CO/W), the rate decreases as CO is evolved. If we suppose that CO release indicates a kind of decomposition of the catalyst, it is not the final product of this decomposition which is the active complex. The maximum of activity is observed right after O_2 introduction, when the system contains the active Al# species which is probably interacting with the tungsten complex. So we attempted to determine by ir and uv spectroscopy the processes occurring at this stage on the tungsten complex.

4. *Spectroscopic Studies*

We have studied by ir and uv spectroscopy the interactions between $W(CO)_5P\phi_3$ and O_2, $W(CO)_5P\phi_3$ and $EtAlCl_2$ and $W(CO)_5P\phi_3$, $EtAlCl_2$, O_2 in order to determine the changes which occurred when the catalyst became efficient.

Infrared results reported here are limited to the carbonyl stretching region (Fig. 4). W–C stretching, W–CO bending and alkyl aluminum vibrations will be discussed in a future paper.

a. Initial $W(CO)_5P\phi_3$

$W(CO)_5P\phi_3$ has C_{4v} symmetry resulting in three infrared allowed CO stretching vibrations, one of E symmetry and two of A_1 symmetry [$A_1^{(1)}$ and $A_1^{(2)}$]. E and $A_1^{(2)}$ modes are accidentally degenerate (*13–15*). In addition, a band of weak intensity is assigned to an ir forbidden vibration of B_1 symmetry which is allowed because of a slight mechanical coupling of the CO stretching motions to the modes of $P(C_6H_5)_3$ (*15*). These vibrational frequencies for solutions of $W(CO)_5P\phi_3$ in *n*-hexane or in chlorobenzene are reported in Table 1. We can see that, in chlorobenzene, the B_1 and E vibrations are shifted to lower frequencies, probably through an electric dipole interaction such as

$$M\text{–}C^{\delta+}\text{—}O^{\delta-}\text{- - - -}C_6H_5Cl.$$

In hexane or in C_6H_5Cl solution, the uv spectrum of $W(CO)_5P\phi_3$ showed an intense band at 235 nm, two strong shoulders at 325 and 350 nm, transitions which can be assigned to charge transfers from W to the π antibonding orbitals of the ligands. The 270 nm shoulder would be a spin-allowed *d–d* transition.

Such an assignment has been made by comparison with the spectrum of $W(CO)_6$. In effect, in such complexes, the main transi-

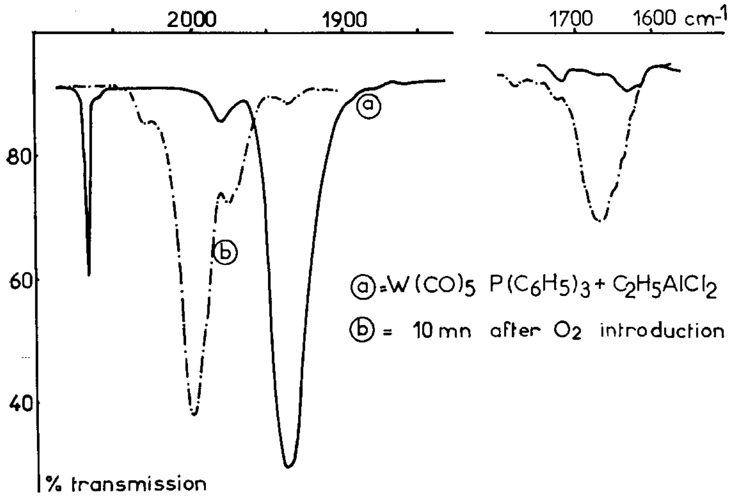


FIG. 4. Infrared spectrum in the ν_{CO} stretching region of $W(CO)_5P\phi_3$. (a) Initial complex; (b) immediately after O_2 introduction for Al/W = 4.

tions arise from charge transfers (CT) from the metal *d* electrons to the empty π antibonding molecular orbitals mostly localized on the CO's (π^*CO) (*16–18*). When a CO ligand is substituted by a poorer π acceptor ($P\phi_3$), the total π back-bonding decreases; the negative charge on the metal increases and the energy of a particular CT decreases (the wavelength increases) (*19–21*). According to such a scheme, we can correlate the 235 and 325 nm transitions of $W(CO)_5P\phi_3$ with the 225 and 288 nm transition of $W(CO)_6$. The exact assignment of the 350 nm maximum would require MO calculations which are out of the scope of this paper. In effect, this band can arise from a CT but also from a spin-forbidden *d–d* transition. In the compounds studied here, we can observe that the *d–d* transition occurs at about the same energy as the CT transitions and so they appear only as shoulders (at 274 and 316–325 nm in $W(CO)_6$).

TABLE 1

Mode of vibration of the C–O stretching	cm^{-1}		
	A_1	B_1	A_1 and E
Solvent C_6H_6Cl	2068	1976	1937
Solvent n-C_6H_{12}	2069	1984	1942

b. *Interactions of $W(CO)_5P\phi_3$ with O_2 or $EtAlCl_2$*

The uv and ir spectra of the starting complex were not modified by O_2 introduction.

Upon action of $EtAlCl_2$ (for molar ratios $Al:W > 1$) in hexane or chlorobenzene solutions, the CT bands were shifted towards higher energies, which would indicate an increase of the positive charge on W connected with an increase of back-bonding from metal to π-accepting ligands. Nevertheless, the ir spectrum did not change significantly in the CO stretching region, indicating no modification of symmetry.

c. *System $W(CO)_5P\phi_3$, O_2, $EtAlCl_2$*

When $(C_2H_5)AlCl_2$ and O_2 interact simultaneously with $W(CO)_5P(C_6H_5)_3$, an immediate and considerable change of the ir spectrum was observed even when scarcely no CO evolution was measured (Fig. 5). The three CO stretching bands were replaced by only one strong band at 1998 cm^{-1} with two weak shoulders at 2030 and 1973 cm^{-1}. At the same time, a broad band appeared at 1667 cm^{-1}.

On the basis of the local symmetry of the carbonyl groups, such a spectrum is attributed to a *trans*-disubstituted complex resulting in one stretching CO vibration of mode 3. Since no CO is evolved, the ligand in the *trans* position to $P(C_6H_5)_3$ cannot be

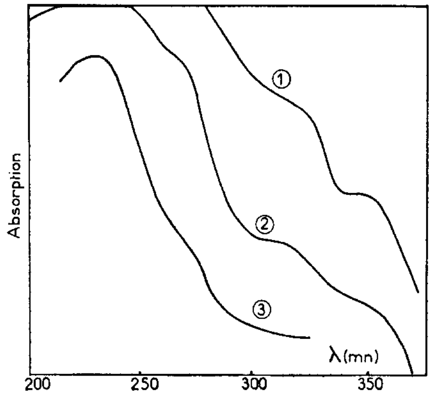
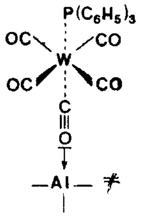


FIG. 5. Ultraviolet spectra of $W(CO)_5P\phi_3$ in C_6H_5Cl at various concentrations: (1) 4×10^{-3} moles liter^{-1}; (2) 2×10^{-3} moles liter^{-1}; (3) 10^{-3} mole liter^{-1}.

substituted: we suggest that it is complexed with the active alkylaluminum according to the following scheme:



Such a complexing is expected to give, for the trans CO, a ν_{CO} between 1600–1700 cm^{-1} (*22–25*) and also to decrease the electronic density on the tungsten atom (and hence to decrease the back-bonding of the metal *d* electrons to the π^* orbitals of CO). In fact we observed a band at 1667 cm^{-1} attributed to the *trans* CO complexed to the Al# species and a band at 1998 cm^{-1} for the E mode of the free carbonyl groups (shift of 55 cm^{-1} towards higher frequencies with respect to the E mode of $W(CO)_5P\phi_3$).

From uv experiments, we verified also that O_2 introduction after action of $EtAlCl_2$ induced immediately an increase of the positive charge of the tungsten (shift of the 320 and 350 nm transitions towards higher energies). Moreover, with time, the solution became colored red and new bands due to a solvent effect on the oxidation products of the aluminum alkyl appeared.

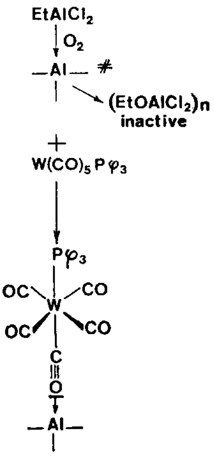
The carbonyl aluminum alkyl intermediate proposed here explains the changes of the $W(CO)_5P\phi_3$ ir and uv spectra. It is important to notice that such a complexing is observed only after O_2 introduction. It is the oxygen which creates a particularly acidic aluminum compound able to interact with the oxygen lone pair of a carbonyl group. This aluminum species could be the peroxyd observed by ir spectroscopy (band at 892 cm^{-1}), but this fact is not proved.

DISCUSSION

It is important to discuss at this stage the actual role played by O_2. The experiments of partial oxidation of $EtAlCl_2$ suggest that it is the aluminum alkyl and not the W compound which is activated by oxygen. An intermediate species produced during the oxidation of the aluminum alkyl would then react (or be complexed) with the tungsten complex.

We have seen that it is right at the beginning of the oxidation that the catalytic system exhibits a very high efficiency. At this stage infrared spectroscopy indicates a complexing of the carbonyl group *trans* to $P\phi_3$ with a Lewis acid and a large decrease of the back bonding of metal *d* electrons to the antibonding orbitals of the CO groups of the square plane. Ultraviolet measurements suggest a simultaneous decay of the charge on W which is also accounted for by the effect of the Lewis acid.

We therefore propose the following scheme:



The active species Al# would act as a Lewis acid able to decrease the electron density on W by complexing to the lone pair of the oxygen of the carbonyl group *trans* to Pϕ_3. This would produce mobility of the carbonyl ligands in the square plane, favoring the coordination of one or more likely two molecules of olefin.

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